

This listing of claims will replace all prior versions, and listings, of claims in the application:

LISTING OF CLAIMS:

Claim 1. (original): Process for the preparation of stable activated derivatives of carbamic acid, comprising at least one protected amino group and an activated carbamic acid function, from an amino acid derivative in which the amino group is protected, comprising:

a) a step of transformation of the -COOH group of the amino acid derivative into a -CON₃ group to obtain an acyl azide,

b) a step of transformation of the -CON₃ group of the acyl azide into a -NCO group to obtain an isocyanate,

c) a step of treating the isocyanate to obtain said stable derivative of carbamic acid.

Claim 2. (original): Process according to claim 1, in which the structure of the carbamic acid derivative is conferred by a group from a compound selected from: N-hydroxysuccinimide, phenol, pentafluorophenol, pentachlorophenol, p-nitrophenol, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2,4-dichloro-6-nitrophenol, hydroxy-1,2,3-benzotriazole, 1-oxo-2-hydroxydihydrobenzotriazine (HODhbt),

7-aza-1-hydroxy-benzotriazole (HOAt), 4-aza-1-hydroxybenzotriazole (4-HOAt), imidazole and tetrazole.

Claim 3. (previously amended): Process according to claim 1, in which the structure of the activated derivative of carbamic acid is conferred by the N-hydroxysuccinimide group.

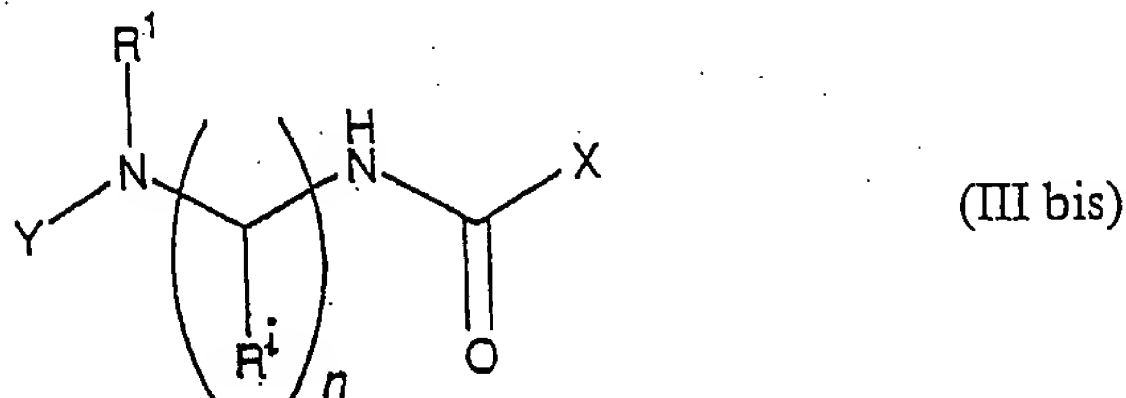
E1 Claim 4. (original): Process for preparation according to claim 1, in which step a) of transformation of the -COOH group to a -CON₃ group is carried out by treatment, with the nitride ion, of an activated derivative of the amino acid in which the amino group is protected.

Claim 5. (previously amended) Process for preparation according to claim 1, in which step a) of the transformation of the -COOH group into a -CON₃ group is carried out by treatment, with hydrazine, of an activated derivative of the amino acid in which the amino group is protected to obtain a hydrazide, which is then subjected to a nitrosation.

Claim 6. (original): Process for preparation according to claim 4, in which step a) of transformation of the -COOH group into a -CON³ group is carried out by treatment of

the mixed anhydride (formed from the amino acid derivative)
with sodium azide.

Claim 7. (original): Compounds of the formula (III
bis)



in which

- E'
- n is a whole number greater than or equal to 1,
 - i is a whole number varying from 2 to n+1,
 - the Y group can be or contain:
 - 1/ a pseudopeptide
 - 2/ an amino acid residue or a chain of amino acids comprising 1 to 10 residues,
 - 3/ a GP group which can be:
 - a protective group selected from: a hydrogen atom, an oxycarbonyl (ROCO), acyl, alkyl, aryl, urea, phthalimide (with $R^1 = \text{O}$), biotin, O_2 (with $R^1 = \text{O}$) group,
 - or such that the GP-N entity forms an NH_2^+ entity,
 - the groups R^1 and R^i can each represent independently from each other: a hydrogen, a halogen, the protected or unprotected side chain of an amino acid selected from natural and synthetic amino acids, a C1-C20 alkyl group

substituted or not, an alkyl group whose cyclic structure contains 5 to 20 carbon atoms, a group OR_a , NH_2 , OH , $-COOR_a$, $-CONHR_a$, $-CONH_2$, $-CH_2COOR_a$, $-CH_2CONHR_a$, $-CH_2CONH_2$,

R_a representing an allyl, benzyl, t-butyl, fluorenylmethyl, alkyl group having 1 to 20 carbon atoms, or an aryl group whose cyclic structure contains 5 to 20 carbon atoms,

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- the X group represents a group conferring on the compound of formula (III bis) a structure of an activated derivative of carbamic acid, which X group is from a compound selected particularly from phenols, if desired substituted with at least one nitro or at least one halogen, or hydroxylamine derivatives, or hydroxy-1,2,3-benzotriazole, 1-oxo-2-hydroxydihydrobenzotriazine (HODhbt), 7-aza-1-hydroxybenzotriazole (HOAt), 4-aza-1-hydroxybenzotriazole (4-HOAt), imidazole and tetrazole,

- the R^1 and R^1 groups can also form a cycle,

provided that the compound of formula (III bis) is different from the following compounds in which:

- $n = 2$, GP = Boc, $R_1 = \text{isobutyl}$, $R_2 = R_3 = H$, X = 4-nitrophenol

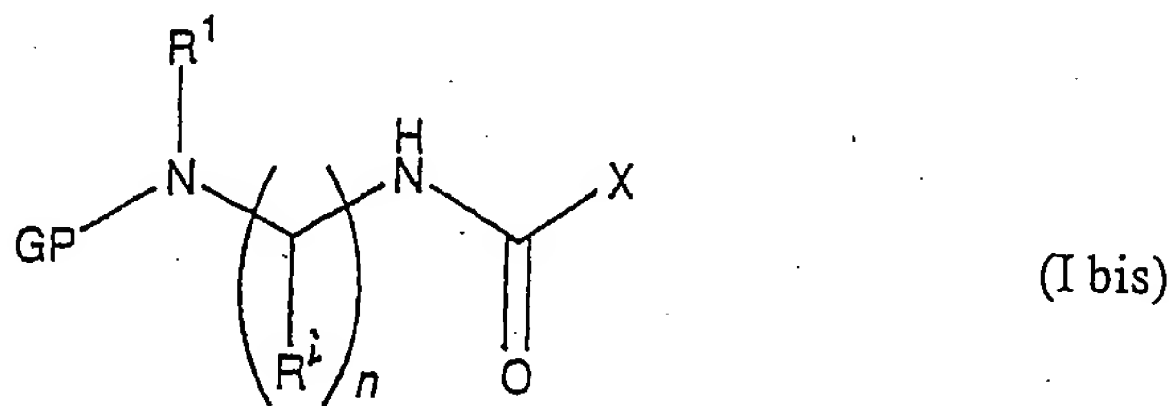
- $n = 2$, GP = Boc, $R_1 = \text{benzyl}$, $R_2 = R_3 = H$, X = 4-nitrophenol

- $n = 2$, $GP = Boc$, $R_1 = CH_2-p-C_6H_4Ot-Bu$, $R_2 = R_3 = H$, X
= 4-nitrophenol
- $n = 2$, $GP = Boc$, $R_1 = H$, $R_2 = R_3 = H$, $X =$
4-nitrophenol.

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Claim 8. (original): Compounds according to claim 7,
in which the X group is from a compound selected from: N-
hydroxysuccinimide, pentafluorophenol, p-nitrophenol and
imidazole.

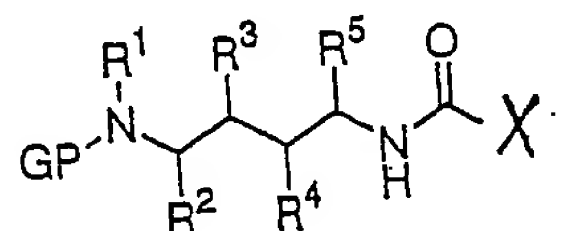
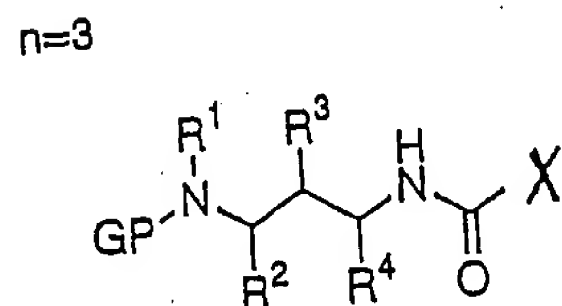
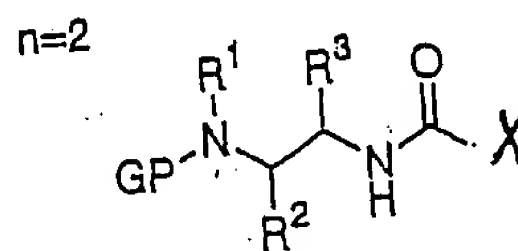
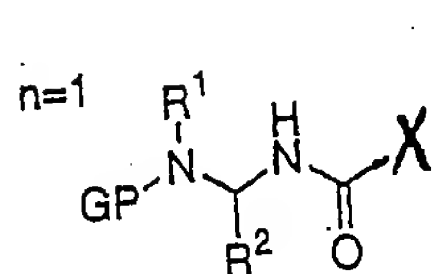
Claim 9. (previously amended): Compounds according to
claim 7, having the formula (I bis)



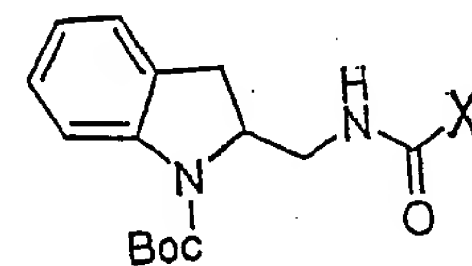
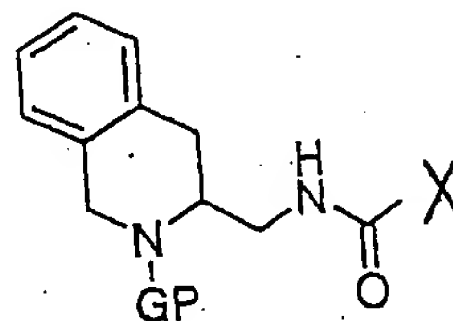
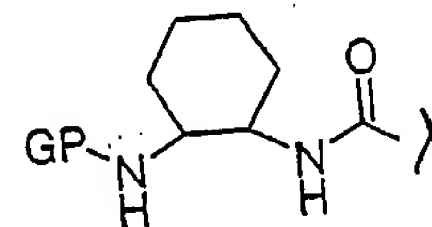
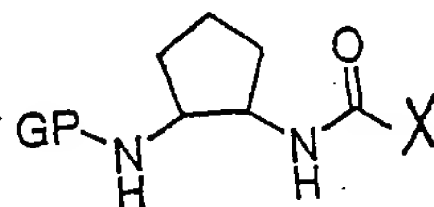
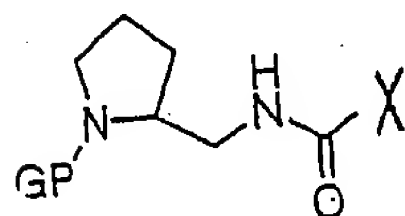
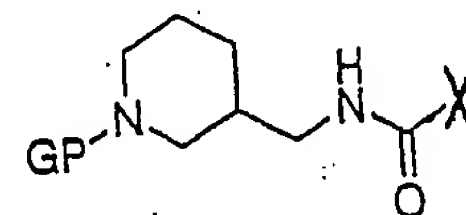
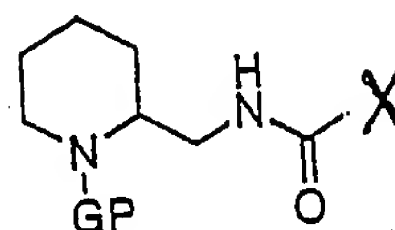
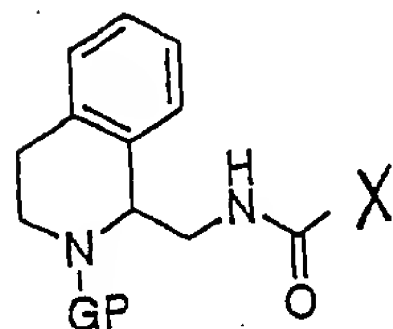
Claims 10 and 11. (Canceled).

Claim 12. (previously amended): Compounds according
to claim 9, having the formula (Ibis) in which $1 < n < 4$, and X is
derived from p-nitrophenol, N-hydroxysuccinimide,
pentafluorophenol, hydroxy-1,2,3-benzotriazole or imidazole,
and GP is an oxycarbonyl group or acyl group.

Claim 13. (original): Compounds according to claim 12, having the following formulas:



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Claim 14. (previously amended): Compounds according to claim 13, in which X is derived from a N-hydroxysuccinimide group.

Claims 15-26 (previously canceled).

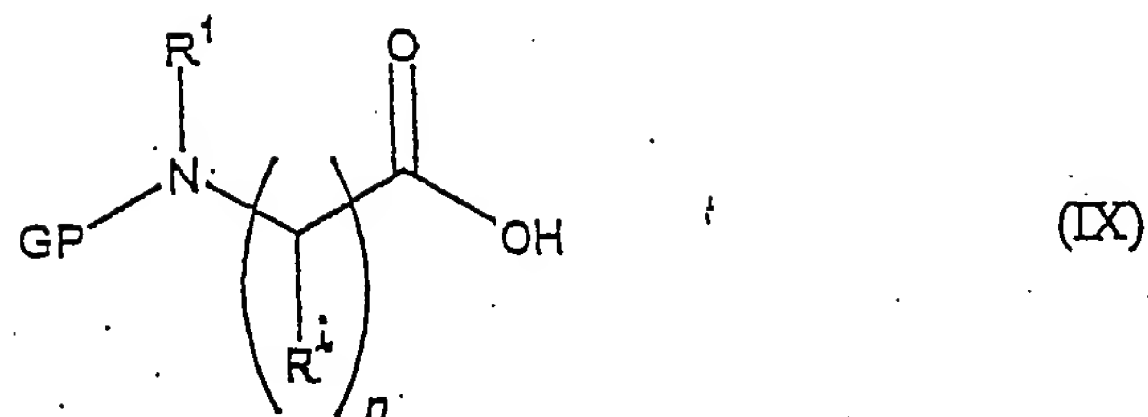
Claim 27. (previously amended) Compounds according to claim 7, in which the aryl group can be substituted with 1 to 6 substituents selected from: alkyl, alkoxy, amine, ester, urea, amide, carboxylic acid, of 1 to 10 carbon atoms, hydroxyl, nitrile, nitro, guanidine, aryl whose cyclic structure contains 5 to 20 carbon atoms, and a halogen atom.

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Claim 28. (previously amended): Compounds according to claim 7, in which the alkyl group is substituted with one or several substituents selected from the groups: -COORh, -CONHRh, -COOH, -OH, -Orh, -NHRh, -NH₂, -NH(CO)Rh, aryl whose cyclic structure contains 5 to 20 carbon atoms, halogen, carbonyl of 1 to 10 carbon atoms, nitrile, guanidine,

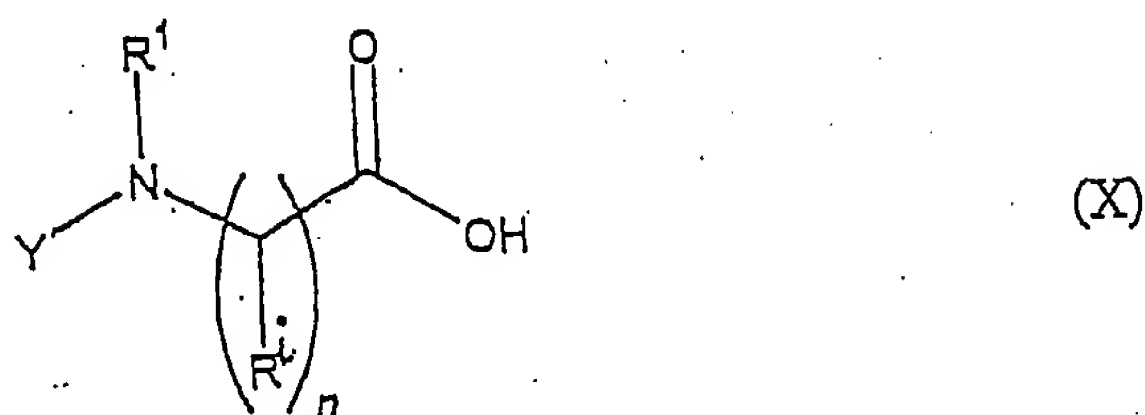
Rh representing an allyl, benzyl, t-butyl, flouroenylmethyl, alkyl group having 1 to 20 carbon atoms, or an aryl group whose cyclic structure contains 5 to 20 carbon atoms.

Claim 29. (previously amended): Process for preparation of derivatives corresponding to the formulas (I bis), (II), (III bis) or (IV) according to claim 7, from respectively,

- compounds of formula (IX) (for compounds of formula (I bis) and (II))



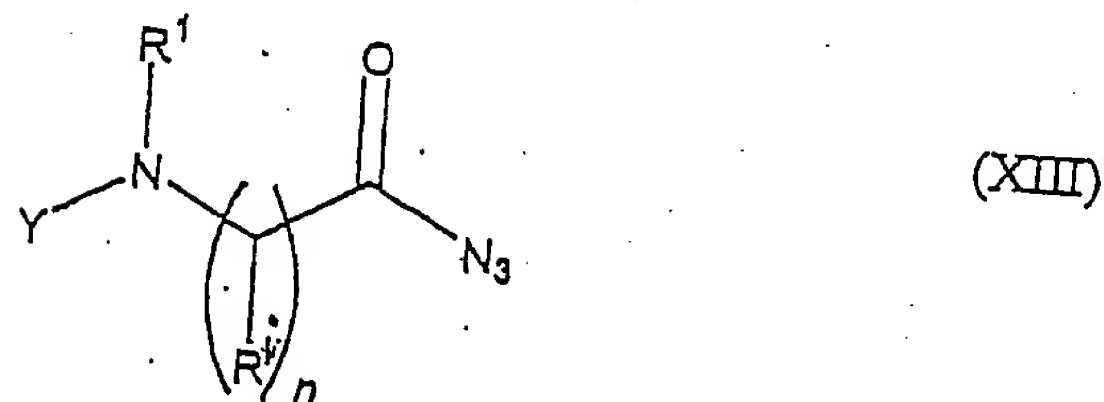
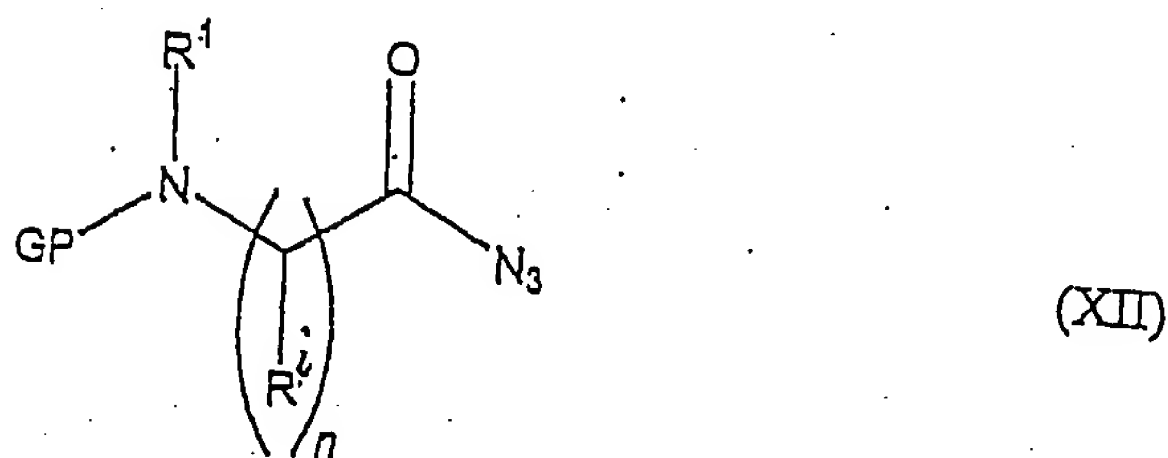
- compounds of formula (X) (for compounds of formula (III bis) and (IV))



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comprising

(a) a step of transformation of acid (IX) or (X) into the corresponding acyl azide (XII) or (XIII) respectively



by a suitable treatment,

(b) a step of transformation of acyl azide (XII) or (XIII) by Curtius rearrangement into the corresponding isocyanate (II) or (IV) respectively,

(c) a step of treatment of isocyanate (II) or (IV), preferably not isolated, under conditions permitting obtaining a carbamic acid derivative of formula (I bis) or (III bis).

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Claim 30. (original): Process for preparation according to claim 29, in which:

- step (a) of transformation of acid (IX) or (X) into the corresponding acyl azide (XII) or (XIII) respectively, is carried out by treatment of the mixed anhydride (formed by the reaction of acid (IX) or (X) with ethyl or isobutyl chloroformate in the presence of a tertiary amine such as NMM (N-methylmorpholine), DIEA (di-isopropylethylamine), or Et₃N in THF (tetrahydrofuran)) with a sodium azide solution,

- step (b) of transformation of acyl azide (XII) or (XIII) into the corresponding isocyanate (II) or (IV), is carried out by heating a solution of acyl azide in a suitable solvent,

- step (c) of treatment of isocyanate (II) or (IV) is carried out, when the isocyanate is in solution, for example in toluene, with one of the derivatives of the following list: N-hydroxysuccinimide, phenol, pentafluorophenol,

E1 pentachlorophenol, p-nitrophenol, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2,4-dichloro-6-nitrophenol, hydroxy-1,2,3-benzotriazole, imidazole, tetrazole, 1-oxo-2-hydroxydihydrobenzotriazine (HODhbt), 7-aza-1-hydroxybenzotriazole (HOAt) and 4-aza-1-hydroxybenzotriazole (4-HOAt), and if desired a base such as pyridine, so as to obtain a carbamic acid derivative of formula (I bis) or (III bis), which is then if desired isolated.

Claims 31-39. (previously cancel).
